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Synthesis, Characterization, and Reactivity of Nickel Hydride Complexes Containing 2,6-$C_6H_3(CH_2PR_2)_2$ (R = *t*Bu, *c*Hex, and *i*Pr) Pincer Ligands

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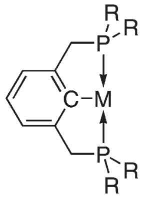
The syntheses and full characterization of nickel hydrides containing the PCP "pincer"-type ligand, where PCP = 2,6-$C_6H_3(CH_2PR_2)_2$ (R = *t*Bu, *c*Hex, and *i*Pr), are reported. These Ni−H complexes are prepared by the conversion of (^{R}PCP)NiCl precursors into the corresponding nickel hydrides by use of appropriate hydride donors. Surprisingly, although the (^{R}PCP)NiCl precursors are quite similar chemically, the conversions to the hydrides were not straightforward and required different hydride reagents to provide analytically pure products. While $NaBH_4$ was effective in the preparation of pure (^{tBu}PCP)NiH, Super-Hydride solution ($LiEt_3BH$ in THF) was required to prepare either (^{cHex}PCP)NiH or (^{iPr}PCP)NiH. Attempts to prepare a Ni−H from (^{Ph}PCP)NiCl with a variety of hydride reagents yielded only the free ligand as an identifiable product. Two of the derivatives, *t*Bu and *c*Hex, have also been subjected to single crystal X-ray analysis. The solid-state structures each showed a classic, near-square planar arrangement for Ni in which the PCP ligand occupied three meridional ligand points with the Ni−H *trans* to the Ni−C bond. The resulting Ni−H bond lengths were 1.42(3) and 1.55(2) Å for the *t*Bu and *c*Hex derivatives, respectively.

Introduction

For many years there has existed significant interest in the preparation and investigation of transition metal complexes that contain rigid, chelated ligands. More specifically, compounds that utilize anionic, tridentate "pincer"-type ligands attached to the metal are currently under study by many groups, and much of the work in this area has been summarized in a recent book devoted to pincer chemistry.[1] This high level of interest is due largely to the ability to finely tune the steric and electronic components of the pincer ligand in a systematic fashion to alter the chemical and physical properties, and hence reactivity, of the metal center. These *trans*-spanning pincer ligands have been shown to be highly effective in preparing stable tridentate complexes of transition metals, including square-planar, d^8 metal species.[2,3] Within the broad class of pincer donor ligands, the PCP pincers [where PCP = 2,6-$C_6H_3(CH_2PR_2)_2$] are of particular interest for use as ligands in catalysis.[2,4] Recent illustrative examples that demonstrate the usefulness of PCP pincers in catalysis can be found in the reports of alkane dehydrogenation,[5−10] olefin metathesis,[11] Heck reaction chemistry,[12−16] transfer hydrogenation,[17] and Aldol condensation chemistry.[18] One attractive feature of the PCP ligand family is the relative



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synthetic ease of R-group substitution on the pincer arms yielding a variety of modified phosphine substituents attached to the bridging atom. While many investigations utilize relatively simple alkyl or aryl derivatives as part of the $-\text{PR}_2$ moiety, significant changes in the electronic nature of the $-\text{PR}_2$ group can easily be accomplished. To illustrate, alterations such as using perfluoro-alkyl and aryl substituents[19,20] or π-accepting N-pyrrolyl groups[21] have been reported. While the most-commonly investigated PCP pincer ligands are based on an aromatic sp^2 phenyl ring backbone, it has also been demonstrated that the carbon ligand component can be part of an sp^3 alkyl chain.[22−26] While these saturated species are indeed technically PCP pincer complexes, in this report we will restrict ourselves to the more commonly used aromatic ring pincers.

We have recently reported the first example of an unambiguous insertion of O_2 into ($^{t\text{Bu}}$PCP)PdH to yield the X-ray crystallographically characterized ($^{t\text{Bu}}$PCP)PdOOH product,[27] and we[28] and others[29,30] have followed this experimental study with detailed computational studies of the mechanism. As part of our search for new selective partial oxidation catalysts that use O_2 gas as the oxidant, we have been interested in expanding the numbers and types of late transition metal hydrides that contain PCP ligands, largely focusing on Ni−H and Pd−H species.[31] In our preliminary investigations we were surprised to discover that there are no pure, well-characterized constituents of the simplest member of this family—the first-row ($^{\text{R}}$PCP)NiH species—that have been reported in the literature. Notably PNP analogues ($^{\text{R}}$PNP)NiH have recently been isolated[32−34] and even characterized by X-ray diffraction.[35] Unfortunately, there is no discussion of the crystallographic parameters or any specific mention of the Ni−H bonds in the structural study. There is only one example mentioned in the literature relating to any aromatic, sp^2 PCP-containing nickel hydride, that being ($^{t\text{Bu}}$PCP)NiH reported in 1976 by Moulton and Shaw.[36] In this study, the authors characterized the compound obtained by the NaBH_4 reduction of ($^{t\text{Bu}}$PCP)NiCl, to which they assigned the (PCP)NiH structure based on IR spectroscopy. The authors were unable to observe the Ni−H resonance by ^{1}H NMR, and suggested an exchange process was possibly responsible for the inability to observe the resonance. Lastly, in related work, we note that an sp^3 carbon-based PCP pincer complex of a nickel hydride has recently been reported by Zargarian and Beauchamp.[37] Similarly to the previous report from Moulton and Shaw,[36] this $(\text{PC}_{sp^3}\text{P})$NiH complex was not isolated as an analytically pure material, but rather as a mixture of the hydride and the free ligand. However, in this case the complex was unambiguously identified by NMR analysis. No structural data were obtained.

As part of our reactivity studies into new pincer-containing Group 10 hydrides we have recently prepared a number of ($^{\text{R}}$PCP)NiH complexes and have crystallographically characterized two ($^{\text{R}}$PCP)NiH derivatives containing either ^{t}Bu (the complex reported previously by Moulton and Shaw[36]) or ^{c}Hex substituents. The hydride complexes were prepared from ($^{\text{R}}$PCP)NiCl precursors and the choice of the specific hydride reagent turned out to be critical to the effective isolation of pure product samples. It is hoped that this report of the preparations of high purity samples of these ($^{\text{R}}$PCP)NiH complexes and their characterization by X-ray crystallography will allow for further exploration of their reactivity.

Experimental Section

General Procedures. All procedures and chemical manipulations were carried out under Ar or vacuum using standard inert atmosphere or Schlenk techniques. High-purity solvents were either used as procured or were dried using standard techniques, and after purification were stored under Ar or in Ar-filled gloveboxes. All reagents were purchased from commercial suppliers (Aldrich and Alfa) and used without further purification. ^{1}H, ^{31}P, and ^{13}C NMR spectra were obtained on a Bruker AMX 250 MHz spectrometer. ^{1}H and ^{13}C spectra are referenced to SiMe_4, while ^{31}P spectra are referenced to external 85% H_3PO_4. Infrared data were obtained on a Bruker Vector 22 instrument using Nujol mulls under an atmosphere of flowing nitrogen gas. Elemental analyses were performed by Columbia Analytical Services, Tucson, AZ. The starting ($^{\text{R}}$PCP)H ligands $1,3\text{-C}_6\text{H}_4[\text{P}(^t\text{Bu})_2]_2$,[38] $1,3\text{-C}_6\text{H}_4[\text{P}(^c\text{Hex})_2]_2$,[39] $1,3\text{-C}_6\text{H}_4[\text{P}(^i\text{Pr})_2]_2$,[40] and $1,3\text{-C}_6\text{H}_4(\text{PPh}_2)_2$[41] were prepared by literature methods. ($^{\text{Ph}}$PCP)NiCl (**1d**) was prepared as reported previously.[42]

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(^{tBu}PCP)NiCl (1a). (^{tBu}PCP)NiCl (**1a**) was prepared with slight modifications to the prior preparation.[36] To an ethanol (10 mL) solution of (^{tBu}PCP)H (1.02 g, 2.6 mmol) was added a solution of $NiCl_2 \cdot (H_2O)_6$ (0.60 g, 2.5 mmol) dissolved in 2 mL of degassed water. The solution was heated to reflux. A golden-yellow precipitate began to form only after 0.5 h. The solution was stirred under low reflux overnight. After cooling, the product was collected by filtration and washed with cold ethanol. **1a** can be recrystallized from a concentrated solution of pentane or hexanes at −35 °C. Yield: 0.73 g (60%). ^{1}H NMR (C_6D_6, 250 MHz): δ 7.0 (t, 1H, $^{3}J_{HH}$ = 7.4 Hz, ArH_p), 6.84 (d, 2H, $^{3}J_{HH}$ = 7.4 Hz, ArH_m), 2.91 (vt, 4H, J^*_{HP} = 6.8 Hz, CH_2), 1.40 (vt, 36H, J^*_{HP} = 12.7 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz) δ 155.7 (t, $^{2}J_{CP}$ = 16.7 Hz, $C_{ar\text{-}i}$), 153.0 (vt, J^*_{CP} = 25.5 Hz, $C_{ar\text{-}o}$), 125.2 (s, $C_{ar\text{-}p}$), 121.8 (vt, J^*_{CP} = 16.7 Hz, $C_{ar\text{-}m}$), 34.9 (vt, J^*_{CP} = 13.4 Hz, PCH_2), 34.3 (vt, J^*_{CP} = 22.7 Hz, P$C(CH_3)_3$), 29.8 (s, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 101.3 MHz) δ 66.9.

(^{cHex}PCP)NiCl (1b). The procedure followed was similar to that of **1a** using the following quantities of reagents: (^{cHex}PCP)H (1.0 g, 2.0 mmol) and $NiCl_2$ $(H_2O)_6$ (0.50 g, 2.1 mmol). Yield: 0.78 g (66%). Anal. Calcd for $C_{32}H_{51}ClNiP_2$: C, 64.94; H, 8.69. Found: C, 65.14; H, 8.81. ^{1}H NMR (C_6D_6, 250 MHz) δ 7.11 (t, 1H, ArH, $^{3}J_{HH}$ = 7.7 Hz), 6.95 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz ArH), 2.86 (vt, 4H, J^*_{HP} = 7.75 Hz, ArCH_2), 2.5−1.0 (m, 44H, cy$H$). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz) δ 158.4 (t, $^{2}J_{CP}$ = 16.7 Hz, $C_{ar\text{-}i}$), 152.9 (vt, J^*_{CP} = 27.4 Hz, $C_{ar\text{-}o}$), 125.3 (s, $C_{ar\text{-}p}$), 122.3 (vt, J^*_{CP} = 18.1 Hz, $C_{ar\text{-}m}$), 33.7 (vt, J^*_{CP} = 25.0 Hz, PCH_2), 32.9 (vt, J^*_{CP} = 20.9 Hz, $C_{cy\text{-}i}$), 28.9 (s, C_{cy}), 27.4−27.3 (m, C_{cy}), 26.8 (s, C_{cy}). ^{31}P{^{1}H} NMR (C_6D_6, 101.3 MHz) δ 51.5.

(^{iPr}PCP)NiCl (1c). The procedure followed was similar to that of **1a** using the following quantities of reagents: (^{iPr}PCP)H (0.785 g, 2.3 mmol) and $NiCl_2$ $(H_2O)_6$ (0.55 g, 2.3 mmol). **1c** was isolated by crystallization from concentrated ethanol solution at −35 °C. Yield: 0.54 g (54%). Anal. Calcd for $C_{20}H_{35}ClNiP_2$: C, 55.66; H, 8.17. Found: C, 55.71; H, 7.95. ^{1}H NMR (C_6D_6, 250 MHz) δ 7.02 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, $C_{ar}H_p$), 6.88 (d, 2H, $^{3}J_{HH}$ = 7.5 Hz, $C_{ar}H_m$), 2.71 (vt, 4H, J^*_{HP} = 7.5 Hz, CH_2), 2.08 (m, 4H, PCH), 1.44 (dvt, 12H, $^{3}J_{HH}$ = 7.7 Hz, J^*_{HP} = 15.9 Hz, CH_3), 0.95 (dvt, 12H, $^{3}J_{HH}$ = 6.9 Hz, J^*_{HP} = 14.0 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz) δ 158.2 (t, $^{2}J_{CP}$ = 16.6 Hz, $C_{ar\text{-}i}$), 152.8 (vt, J^*_{CP} = 27.0 Hz, $C_{ar\text{-}o}$), 125.3 (s, $C_{ar\text{-}m}$), 122.4 (vt, J^*_{CP} = 17.7 Hz, $C_{ar\text{-}m}$), 32.6 (vt, J^*_{CP} = 25.0 Hz, PCH_2), 23.5 (vt, J^*_{CP} = 21.2 Hz, PCH), 18.9 (s, CH_3), 18.1 (s, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 101.3 MHz) δ 60.2.

(^{tBu}PCP)NiH (2a). 2a was prepared by a slight modification of the previous literature procedure.[36] **1a** (0.08 g, 0.16 mmol), and $NaBH_4$ (0.06 g, 1.5 mmol) were mixed in a flask to which 15 mL of a degassed mixture of benzene and ethanol (1:1) was added. The solution was stirred overnight and then another 0.20 g of $NaBH_4$ was added. Stirring was continued for approximately 3 h after which degassed water was added. The solvent was removed under vacuum, and the product extracted into benzene (10 mL) and filtered. The solvent was again removed under vacuum, and pentane was added. After filtering and concentrating the solution, the product crystallized as golden-brown blocks at −35 °C. Yield 0.052 g (72%). Anal. Calcd for $C_{24}H_{44}NiP_2$: C, 63.60; H, 9.78. Found: C, 63.79; H, 10.12. ^{1}H NMR (C_6D_6, 250 MHz) δ 7.22 (m, 3H, ArH), 3.31 (vt, 4H, J^*_{HP} = 8.0 Hz, ArCH_2), 1.26 (vt, 36H, J^*_{HP} = 12.9 Hz, CH_3), −10.0 (t, 1H, $^{3}J_{HP}$ = 52.8 Hz, NiH). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz) δ 152.7 (vt, J^*_{CP} = 27.3 Hz, $C_{ar\text{-}o}$), 124.7 (s, $C_{ar\text{-}p}$), 121.0 (vt, J^*_{CP} = 17.3 Hz, $C_{ar\text{-}m}$), 38.0 (vt, J^*_{CP} = 21.5 Hz, PCH_2), 33.6 (vt, J^*_{CP} = 16.3 Hz, P$C(CH_3)_3$), 29.8 (s, CH_3). ^{31}P{^{1}H} NMR (C_7D_8, 101.3 MHz) δ 99.8 ppm. IR (Nujol mull) $\nu_{(NiH)}$ 1754 cm^{-1}.

(^{cHex}PCP)NiH (2b). A sample of **1b** (0.083 g, 0.14 mmol) was dissolved in 8 mL of toluene and cooled to 0 °C in an ice bath. Super-Hydride solution (0.18 mL, 0.18 mmol, 1 M solution of $LiEt_3BH$ in THF) was added dropwise via syringe. The solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum, and the product extracted in 15 mL of pentane. The slightly cloudy golden solution was filtered, and the filtrate concentrated. Cooling to −35 °C gave the product as orange/brown crystals. Yield: 0.055 g (70%). Anal. Calcd for $C_{32}H_{52}NiP_2$: C, 68.95; H, 9.40. Found: C, 68.94; H, 9.58. ^{1}H NMR (C_6D_6, 250 MHz) δ 7.21 (m, 3H, ArH), 3.17 (vt, 4H, J^*_{HP} = 7.75 Hz, ArCH_2), 2.2−1.0 (m, 44H, cy$H$), −9.9 (t, 1H, $^{2}J_{HP}$ = 55.5 Hz, Ni-H). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz) δ 151.6 (vt, J^*_{CP} = 27.0 Hz, $C_{ar\text{-}o}$), 125.0 (s, $C_{ar\text{-}p}$), 121.2 (vt, J^*_{CP} = 17.5 Hz, $C_{ar\text{-}m}$), 38.6 (vt, J^*_{CP} = 24.6 Hz, PCH_2), 34.7 (vt, J^*_{CP} = 23.3 Hz, $C_{cy\text{-}i}$), 29.3 (s, C_{cy}), 27.4−27.3 (m, C_{cy}), 26.8 (s, C_{cy}). The $C_{ar\text{-}I}$ was not observed. ^{31}P{^{1}H} NMR (C_6D_6, 101.3 MHz) δ 66.9 ppm. IR (Nujol mull) $\nu_{(NiH)}$ 1727 cm^{-1}.

(^{iPr}PCP)NiH (2c). This compound was prepared and isolated similarly to **2b**, with the following quantities used: **1c** (0.066 g, 0.15 mmol), and Super-Hydride solution (0.2 mL, 0.2 mmol, 1 M solution in THF). The product crystallizes as yellow/brown needles. Yield: 0.33 g (55%). Anal. Calcd for $C_{20}H_{36}NiP_2$: C, 60.49; H, 9.14. Found: C, 60.50; H, 8.99. ^{1}H NMR (C_6D_6, 250 MHz) δ 7.24 (m, 3H, ArH), 3.15 (vt, 4H, J^*_{HP} = 7.75 Hz, ArCH_2), 1.92 (m, 4H, CH), 1.23 (dvt, 12H, $^{3}J_{HH}$ = 7.1 Hz, J^*_{HP} = 15.5 Hz, CH_3), 0.97 (dvt, 12H, $^{3}J_{HH}$ = 6.9 Hz, J^*_{HP} = 13.8 Hz, CH_3), −9.9 (t, 1H, $^{2}J_{HP}$ = 55.6 Hz, Ni-H). ^{13}C{^{1}H} NMR (C_6D_6, 64.9 MHz) δ 151.6 (vt, J^*_{CP} = 27.8 Hz, $C_{ar\text{-}o}$), 125.0 (s, $C_{ar\text{-}p}$), 121.3 (vt, J^*_{CP} = 17.2 Hz, $C_{ar\text{-}m}$), 37.9 (vt, J^*_{CP} = 24.6 Hz, PCH_2), 25.1 (vt, J^*_{CP} = 23.7 Hz, PCH), 20.0 (s, CH_3), 18.8 (s, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 101.3 MHz) δ 78.2 ppm. IR (Nujol mull) $\nu_{(NiH)}$ 1736 cm^{-1}.

X-ray Crystallography. Crystallographic data for **2a** and **2b** were collected on a standard Bruker X8 APEX2 CCD-based X-ray diffractometer equipped with an Oxford Cryostream 700 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power (50 kV, 30 mA). Crystals were mounted on nylon cryoloops obtained from Hampton Research using Paratone-N oil. X-ray data collection was performed at 228(2) K for both samples. The data collection and processing utilized the Bruker APEX2 suite of programs, and the SADABS program was used to correct for Lorentz polarization effects and absorption.[43] The two structures were solved by direct methods and refined by full-matrix least-squares calculations based on F^2 using the Bruker SHELXTL (version 6.12) program.[44] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms attached to carbon were placed in calculated positions. The hydrogen atoms attached to the Ni atoms in both structures were located, and more extensive discussion on this topic is given in the text below. Additionally, in the case of **2b** it was apparent there were disordered solvent molecules present, and so the data were treated by SQUEEZE.[45] Corrections of the data by SQUEEZE (4 void spaces of 794 Å^3 with 34 electrons per void) were consistent with two molecules of highly disordered THF solvent with roughly 50% occupancy. Thermal ellipsoid plots were prepared using the Diamond (version 3.1f) software.[46] Crystallographic data collection parameters and refinement data are collected in Table 1.

Results and Discussion

Preparation and Characterization of (^{R}PCP)NiCl (1a−d) Species. To prepare the desired (^{R}PCP)NiH complexes, we first prepared the corresponding (^{R}PCP)NiCl precursors. The free ligand compounds of interest, (^{R}PCP)H, where R = ^{t}Bu, ^{c}Hex, ^{i}Pr, and Ph, were already

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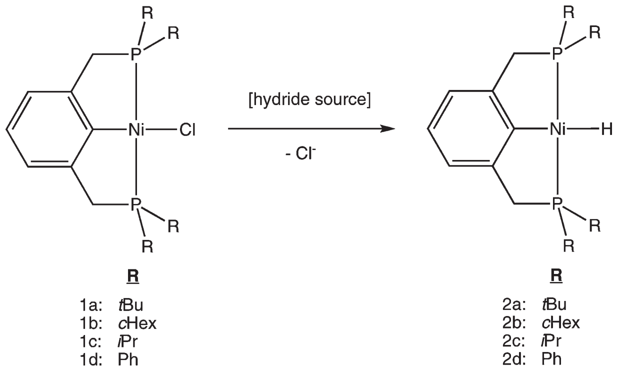
Table 1. Crystallographic Data and Parameters for Complexes **2a** and **2b**

	2a	**2b**
empirical formula	$C_{24}H_{44}NiP_2$	$C_{32}H_{52}NiP_2$
Fw	453.24	557.39
T, K	228(2)	228(2)
cryst size (mm)	0.48 × 0.44 × 0.34	0.51 × 0.46 × 0.34
cryst syst	tetragonal	orthorhombic
space group	$I4(1)cd$	$Ccca$
a, Å	16.1519(4)	19.960(2)
b, Å	16.1519(4)	26.455(3)
c, Å	19.1801(5)	27.789(3)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
Volume, Å^3	5003.8(2)	14674(3)
Z	8	16
calc. density, g/cm^3	1.203	1.009
μ (Mo Kα), mm^{-1}	0.910	0.631
R1[$I > 2\sigma(I)$][a]	0.0305	0.0408
wR2[$I > 2\sigma(I)$][b]	0.0766	0.1153

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Scheme 1. Preparation of Pincer-Containing Nickel Hydrides



reported in the literature,[38−41] and a limited number of (^{R}PCP)NiCl salts were also known.[36,42]

Moulton and Shaw had previously synthesized (^{tBu}PCP)NiCl in 54% yield by reacting (^{tBu}PCP)H directly with $NiCl_2 \cdot 6H_2O$ in a mixed aqueous/ethanolic solution.[36] We followed this general synthetic procedure for the preparation of **1b-d** with the slight modifications mentioned in the Experimental Section. While the ^{t}Bu- and Ph-substituted nickel chlorides are known compounds,[36,42] the ^{c}Hex and ^{i}Pr derivatives have not been reported previously. The new compounds **1b** and **1c** were obtained in moderate yields (54−66%) after recrystallization, and characterized by elemental analysis and multinuclear NMR. In both cases, the ^{31}P NMR resonance appears as a singlet in the same region as in **1a**, and in the ^{1}H NMR spectra the bridging CH_2-groups appear as a virtual triplet, indicating coupling to both P arms. The strong coupling creating this virtual triplet is indicative of the coordination of both arms of the (^{R}PCP)-ligand to the metal. While spectroscopic data were consistent with square-planar (^{R}PCP)NiCl structures with *trans*-spanning phosphines (as in **1a** and **1d**), we recently performed a single crystal X-ray analysis on **1a** to confirm its structure.[47]

Preparation and Characterization of (^{R}PCP)NiH (2a−c) Species. Our primary motive in preparing the (^{R}PCP)NiCl salts was to convert them to the corresponding hydrides, (^{R}PCP)NiH (Scheme 1). The conversions of various other metal halides containing PCP ligands to their corresponding hydrides appear in the literature and can be quite facile.[36,48−54] The two most common sources of hydride employed previously with metal pincer halides appear to be $LiAlH_4$ and $NaBH_4$. Analytically pure **2a** was prepared from (^{tBu}PCP)NiCl in 72% yield using $NaBH_4$. The proton-decoupled ^{31}P NMR spectrum of the crude product indicated that **2a** was the only P-containing product present, and after recrystallization from pentane, orange-brown single crystals suitable for single-crystal X-ray analysis were obtained. Notably, Moulton and Shaw were not able to obtain a pure sample of 2a.[36] With a pure sample of **2a** in benzene-d_6, the Ni−H resonance clearly appears as a clean triplet at δ 10.0 ppm ($^{2}J_{P-H}$ = 52.8 Hz) in the ^{1}H NMR spectrum. It is possible that the impurities present in the earlier work caused an exchange process to occur at room temperature, thus significantly affecting their ^{1}H NMR spectrum. Additionally, the Ni−H stretch of high purity **2a** was observed in the IR spectrum at 1754 cm^{-1}, slightly different from the previously reported 1730 cm^{-1}.[36] It was also possible to prepare **2a** using a slight molar excess of $Li(Et_3BH)$ (Super-Hydride solution) in THF as the source of hydride, although ^{1}H NMR analysis indicated that **2a** was not formed cleanly. Even with excess $Li(Et_3BH)$ the reaction did not appear to go to completion, as indicated by the continued presence of starting material **1a** in the crude product mixture. In solution, **2a** reacted relatively rapidly with air and was thus stored under inert atmosphere.

Unlike **1a**, we found it was not possible to prepare the hydride with $NaBH_4$ when using the ^{c}Hex derivative **1b**. Reaction of **1b** with $NaBH_4$ at room temperature did not produce **2b**, but rather a broadened signal was present in the ^{1}H NMR spectrum that was consistent with a [(^{cHex}PCP)Ni][BH_4] type complex containing bridging hydrides.[53] Under more forcing conditions of overnight refluxing, a $NaBH_4$ solution with **1b** afforded only a small amount (<5%) of the desired product as determined by ^{31}P NMR, and the broadened signal seen previously in the ^{1}H NMR spectrum at room temperature was also present. Use of $LiAlH_4$ at room temperature gave the uncomplexed (^{cHex}PCP)H ligand as the only identifiable product. Additionally, when K($^{s}Bu_3$BH) in THF (K-Selectride solution) was used, we again obtained only small amounts (<25%) of the desired product **2b**, in insufficient yields to warrant further investigation. However, changing the reductant to Super-Hydride solution in THF/toluene at room temperature overnight, followed by removal of solvents and crystallization from pentane at −35 °C, afforded **2b** in 70% yield. The orange-brown

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crystals obtained from pentane were suitable for single crystal X-ray diffraction. The ^{1}H and ^{31}P NMR spectra were consistent with a square-planar ($^{c\mathrm{Hex}}$PCP)NiH structure with *trans*-P arms. Again, as with **2a**, the Ni−H resonance of **2b** was clearly observable in the ^{1}H NMR as a triplet at δ −9.9 ppm ($^2J_{\mathrm{P-H}}$ = 55.5 Hz). The single ^{31}P {^{1}H} signal was found at 66.6 ppm. Additionally, in the IR spectrum the Ni−H stretch was observed at 1727 cm^{-1}. As with **2a**, **2b** was stored under inert atmosphere as it was reactive to air in solution.

For the ^{i}Pr derivative **1c**, the use of $NaBH_4$ again proved ineffective in converting the Ni−Cl bond to a Ni−H bond. Ultimately, the experimental results obtained using **1c** mirrored closely those of **1b**: the use of Super-Hydride solution cleanly afforded **2c** after recrystallization as yellow-brown crystals in similar, but slightly lowered, yield (55%). Unfortunately, we were unable to grow single crystals of **2c** that were of sufficient quality for X-ray diffraction. However, we were able to show by other spectroscopic methods that the conversion of **1c** to analytically pure **2c** had occurred cleanly. Again, the ^{31}P NMR spectrum showed only a single resonance at 78.2 ppm, indicating the symmetrical nature of the two P(^{i}Pr)$_2$ arms. In the ^{1}H NMR spectrum, the ^{i}Pr group was easily identifiable, as the methyl group protons appear in this ($^{i\mathrm{Pr}}$PCP)NiH structure as a doublet of virtual triplets, as has been seen earlier by Campora in a ($^{i\mathrm{Pr}}$PCP)Ni(ONO_2) complex.[55] The methine proton is found in **2c** as a symmetrical multiplet. Upon P-decoupling, the doublets of virtual triplets collapse to simple doublets. The Ni−H resonance is observed as a triplet at δ −9.9 ppm ($^2J_{\mathrm{P-H}}$ = 55.6 Hz). As well, the Ni−H bond stretch is found in the IR at 1736 cm^{-1}.

Quite surprisingly, all attempts to convert the phenyl derivative **1d** to the corresponding hydride **2d** were unsuccessful. Use of any of the hydride reagents mentioned above led to immediate darkening of the solution and apparent decomposition of **1d**. This was somewhat surprising as the reducing ability of the different reagents varied over a significant range. However, in no case did we observe any product that could be shown to contain both a PCP ligand and a nickel hydride. We also utilized an additional hydride source, $NaBH_3CN$ in THF solution, that did not appear to immediately decompose **1d** at room temperature. However, NMR evaluation of the crude solution did not contain any resonances that could be attributed to the nickel hydride. Interestingly, a recent paper from Liang has reported the X-ray structures of related ($^{\mathrm{R}}$PNP)NiH compounds prepared by oxidative addition of the ($^{\mathrm{R}}$PNP)H ligand to Ni(COD)$_2$.[35] Liang noted that while the diphenylphosphino-substituted PNP nickel hydride could be generated in solution and identified via spectroscopic means, it could not be isolated under the conditions used, as the COD byproduct inserted into the nickel hydride to form an Ni alkyl complex. Only the PNP nickel hydrides prepared by Liang that contained alkyl-substituted phosphines could be isolated and characterized fully, results that are quite similar to ours.

Crystallographic Results. Solid-state X-ray diffraction data exist for several PCP-containing transition metal hydrides; however, there are no examples of ($^{\mathrm{R}}$PCP)NiH complexes that have been structurally characterized. This is a significant omission, as coordination complexes containing Ni−H bonds have been invoked in a wide number of academic and industrial catalytic processes.[56−65] Interestingly, a search of the Cambridge Structural Database (CSD, November, 2008 update)[66] indicates a paucity of terminal hydrides attached to square-planar, tetra-coordinate Ni ions, regardless of the other ligands present. Fortunately, from concentrated pentane solutions held at −35 °C we were able to grow single crystals of both **2a** and **2b** suitable for X-ray analysis. We note that while the analyzed crystal of **2a** darkened significantly during the data acquisition period and may have experienced degradation while in the X-ray beam at −45 °C, the crystal was of high enough quality to complete the analysis. A summary of X-ray data and parameters for both compounds is given in Table 1.

The molecular structure of the ^{t}Bu derivative **2a** is shown in Figure 1, which also includes the important bond lengths and angles found in the structure. The overall structure of **2a** is consistent with the classic Group 10 pincer structure, a slightly distorted square-planar coordination geometry for Ni containing two *trans*-phosphine arms. The other two coordination sites to Ni are filled with the C(1) of the phenyl ring and the hydride, H(1) (vide infra). The four coordinating atoms bound to nickel are coplanar with Ni(1), and form a plane that is twisted by approximately 8° from the plane formed by the six aromatic ring carbons. This creates a C_2 rotational axis in **2a** through the H(1)−Ni(1)−C(1)-C(4) atoms, along the *c* axis that is present. The P(1)−Ni(1)−P(1) angle is 173.54 (3)°, which is much closer to linearity than has previously been seen in the related complexes ($^{i\mathrm{Pr}}$PCP)NiX (X = -I,[67] -OH,[55] NH$_2$,[68] or OCH$_3$[68]), ($^{c\mathrm{Hex}}$PCP)NiBr,[69] ($^{\mathrm{Ph}}$PCP) NiBr,[70] and ($^{t\mathrm{Bu}}$PCP)NiCl[47] in which the P−Ni−P angle ranges from 165.1 to 169.7°. One might expect that as the P−Ni−P angle increases toward linearity in this family of compounds that the Ni−C bond would appreciably shorten to accommodate this widening. However, the

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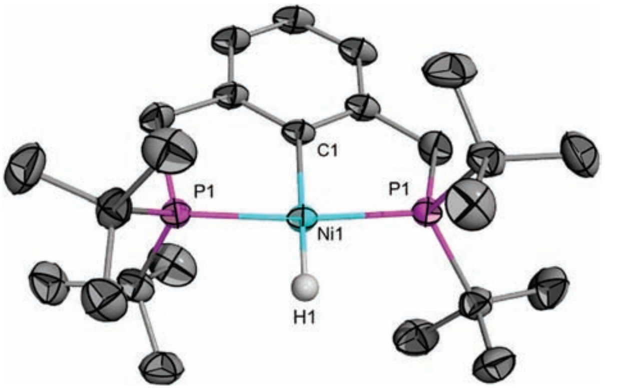

Figure 1. Molecular structure of **2a** (50% ellipsoids). The H atoms attached to carbon are omitted for clarity. Important bond lengths (Å) and angles (deg) are as follows: Ni(1)−H(1) 1.42(3), Ni(1)−P(1) 2.1278(3), Ni(1)−C(1) 1.920(2), C(1)−Ni(1)−H(1) 180.000(5), C(1)−Ni(1)−P(1) 86.768(14), P(1)−Ni(1)−H(1) 93.232(15), P(1)−Ni(1)−P(1) 173.54(3).

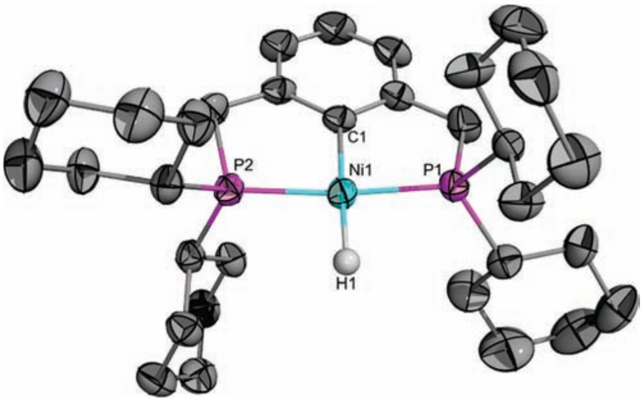

Figure 2. Molecular structure of **2b** (50% ellipsoids). The H atoms attached to carbon are omitted for clarity. Important bond lengths (Å) and angles (deg) are as follows: Ni(1)−H(1) 1.55(2), Ni(1)−P(1) 2.1248(4), Ni(1)−P(2) 2.1300(4), Ni(1)−C(1) 1.9263(14), C(1)−Ni(1)−H(1) 176.7(8), P(1)−Ni(1)−P(2) 173.207(17), C(1)−Ni(1)−P(1) 86.41(5), C(1)−Ni(1)−P(2) 86.90(5), P(1)−Ni(1)−H(1) 92.2(8), P(2)−Ni(1)−H(1) 94.5(8).

Ni−C bond length in **2a** is 1.920(2) Å, the midpoint within the range of Ni−C bonds found in these related (^{R}PCP)NiX compounds, which has a range of Ni−C bond lengths from 1.908−1.931 Å. Additionally, this suggests that there is no significant *trans* influence present, as the two ligands with the largest difference in σ-donor ability, -H and -OH, result in identical Ni−C bond lengths *trans* to these ligands.[71] The P(1)−Ni(1) bond length (2.1278(3) Å) is somewhat shorter than the P−Ni bonds measured in the previously characterized (^{R}PCP)NiX pincer complexes listed above. The reduction in bond length of ~0.05 Å in **2a** can be attributed to the smaller ligand (X = H) present in **2a** relative to the other ligands (X = -I, -Br, -Cl, -OH, -NH_2, or −OCH_3). This smaller ligand explanation can also be utilized to help understand why the P(1)−Ni(1)−P(1) bond angle widens and is significantly closer to linearity in **2a** than in the other related compounds. Other bond angles within the primary coordination sphere of Ni in **2a** are similar to other (^{R}PCP)NiX species, and need not be discussed further. However, location of the hydride attached to Ni proved somewhat more challenging.

In the search of the CSD (November, 2008 update)[66] for prior structurally characterized, tetra-coordinated nickel atoms containing a terminal hydride ligand we found only six examples, none of which were closely related structurally to **2a** (see Supporting Information for search details). The Ni−H bonds measured in these compounds ranged from 1.327 to 1.654 Å, a wide series that indicates the variety of ligand environments and ionic charges present within this small group of compounds. In solving the structure of **2a**, all H atoms were refined in calculated positions with the exception of the Ni−H bond. We initially allowed the hydrogen attached to the nickel atom to vary in position and U_{iso}. However, when doing this, two large residual electron density peaks appeared, located on a symmetry axis around nickel, at a distance of approximately 0.8−0.9 Å from Ni. The U_{iso} value tended to be small and even negative, indicating there was more electron density present than a hydrogen atom should normally allow. We then fixed U_{iso} at a small value (0.02), and this led to a final solution with a chemically unrealistic value of 0.92 Å for the Ni−H bond length. We believe that the large residual electron density is likely due to the Fourier series truncation effect because of a lack of collected data,[72] as the two residual electron density peaks are located on a symmetry axis containing the Ni atom. To solve this issue, we initially constrained the Ni−H bond length to be 1.50 Å, and then allowed the Ni−H bond to vary during refinement. The value of the Ni−H bond length resulting from this model treatment in **2a** settled at 1.42(3) Å, well within the range seen earlier for other Ni−H bonds attached to four-coordinate Ni atoms, and is consistent with the value obtained for **2b** (vide infra).

The molecular structure of the related ^{c}Hex derivative **2b** is shown in Figure 2, along with pertinent bond distances and angles. The overall structural features of **2b** appear largely similar to **2a**; however, there are some significant differences in details between the two compounds. First, the molecular structure of **2b** is of lower symmetry than is seen in **2a**, as **2b** does not contain a C_2 rotational axis or any other symmetry elements to interrelate the two halves of the molecule. Unlike **2a**, the four coordinating atoms [P(1), P(2), C(1), and H(1)] attached to Ni(1) in **2b** are not coplanar with Ni(1). This lack of symmetry leads to slightly different Ni(1)−P(1) and Ni(1)−P(2) bond lengths [2.1248(4), 2.1300(4) Å], as well as unique P(1)−Ni(1)−H(1) and P(2)−Ni(1)−H(1) bond angles [92.2(8), 94.5(8)°]. The Ni(1)−C(1) bond length of 1.9263(14) Å seen in **2b** is very similar to the Ni−C bond seen in **2a** (1.920(2) Å). As was seen above, the P(1)−Ni(1)−P(2) bond angle of 173.207(17)° of **2b** is opened up more toward linearity than has been seen with the previously mentioned structures of (^{R}PCP)NiX (where X ≠ H). The C(1)−Ni(1)−H(1) bond angle also approaches linearity at 176.7(8)°.

Unlike the situation above with **2a**, in the case of **2b** there were no crystallographic issues dealing with locating the hydrogen atom attached to Ni. The Ni−H bond length was found to be 1.55(2) Å, somewhat longer than the one found in **2a**, but quite reasonable relative to

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Ni$-$H bond lengths found in previously studied Ni$-$H compounds.

Summary

We report herein the syntheses and initial single crystal X-ray structural characterizations of nickel hydrides containing the *trans*-spanning ^{R}PCP-pincer ligand, where R = *t*Bu or *c*Hex. The structures each showed a classic, near-square planar arrangement for Ni in which the PCP ligand occupied three meridional ligand points and the Ni$-$H was *trans* to the Ni$-$C bond. The resulting Ni$-$H bond lengths were found to be 1.42(3) and 1.55(2) Å for the *t*Bu and *c*Hex derivatives, respectively. The *i*Pr derivative could also be prepared cleanly, although its solid-state structure could not be determined. These complexes were prepared by the conversion of the precursor (^{R}PCP)NiX compounds in the hydrides by use of suitable hydride donors. Surprisingly, although the (^{R}PCP)NiX precursors are quite similar, the conversions to the hydrides were not straightforward and required different hydride reagents to effect the transformations. The common reducing agent $NaBH_4$ was effective only in the (^{tBu}PCP)-containing complex. Super-Hydride solution ($LiEt_3BH$ in THF) was required to prepare the *c*Hex- and *i*Pr-containing derivatives. Use of $NaBH_4$ or $LiAlH_4$, both common reducing agents, yielded products consistent with overreduction of the Ni. Attempts to reduce the (^{Ph}PCP)-derivative yielded only the free ligand as an identifiable product.

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Supporting Information Available: The search parameters used and a listing of results obtained for previous Ni$-$H containing complexes in the Cambridge Structural Database are given. As well, crystallographic data in CIF format for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.